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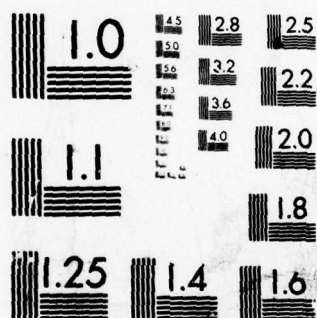UNCLASSIFIED   AEROCHEM-TP-388   AFOSR-TR-79-0941   NL

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Chemical electronic transition lasers

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This work addressed the need to discover, characterize, and understand highly efficient metal atom/oxidizer chemiluminescent reactions for their potential as chemical electronic transition laser (CETL) pumps. Efforts concentrated on the reactions of the Group IVA elements Sn and Ge with N_2O. Overall rate coefficients, photon yields, and quenching coefficients were measured and mechanistic insights were obtained. Techniques for such studies were further developed and critically compared to those in use elsewhere. The experiments were performed in high-temperature fast-flow

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reactors (HTFFR) which allow for independent control of temperature, total pressure, and reactant and quencher concentrations and are thus uniquely suited to kinetic measurements. The detailed results are contained in a number of publications, the abstracts of which are included. It is concluded that Sn/N_2O is the most attractive CETL candidate of the Group IVA element/N_2O reactions but that, as a practical device, it may face development difficulties due to product quenching.

AeroChem TP-388

KINETIC SPECTROSCOPY OF METAL ATOM/OXIDIZER CHEMILUMINESCENT REACTIONS FOR LASER APPLICATIONS

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July 1979

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I. INTRODUCTION - STATEMENT OF WORK

The objectives of this study were to:

1. Provide information on chemiluminescent reactions useful to electronic transition chemical laser development.

2. Perform research of fundamental significance which will enhance our general understanding of high photon yield chemiluminescent reactions and allow generalizations to be made for further selection of laser pumping reactions.

To these ends experimental effort concentrated on the reactions of the Group IVA elements Sn and Ge with N_2O. Overall rate coefficients, photon yields, and quenching coefficients were measured and mechanistic insights were obtained. Techniques for such studies were further developed and critically compared in an extensive review. The experiments were performed in high-temperature fast-flow reactors (HTFFR) which allow for independent control of temperature, total pressure, and reactant and quencher concentrations and are thus uniquely suited to kinetic measurements. Independent control of heating zones in the HTFFR allows a high-temperature (e.g., $\approx$ 1700 K) metal atom source section to be combined with a reaction zone whose temperature can range from about 300-1900 K.

The progress can best be judged on the basis of the abstracts of the publications which have resulted from this work (Section II). These publications emphasize the fundamental kinetic spectroscopic aspects of the work. The chemical electronic transition laser (CETL) implications of these results are discussed somewhat more explicitly in Section III.

II. CUMULATIVE CHRONOLOGICAL LIST OF PUBLICATIONS

1. A. Fontijn and W. Felder, "HTFFR Kinetics Studies: A Chemiluminescence Titration Method for the Determination of Absolute Sn Concentrations," Chemical Physics Letters 47, 380-382 (1977).

Absolute gas phase Sn concentrations in the range $1 \times 10^{13} \leq [Sn] \leq 1 \times 10^{14}$ ml^{-1} have been determined utilizing a technique based on the rapid (at $T \geq 900$ K) titration reaction $Sn + NO_2 \to SnO + NO$ ($k(900-1100$ K) $\approx 1 \times 10^{-10}$ ml molecule^{-1} s^{-1}) and the chemiluminescent indicator reaction $Sn + N_2O \to SnO + N_2 + h\nu$ (SnO $a^3\Sigma-X^1\Sigma$).

2.* A. Fontijn and W. Felder, "HTFFR Studies of the Kinetics of Chemilumin-
   escence Emitter Formation and Quenching in Metal Atom Oxidation Reactions,"
   Electronic Transition Lasers II, L.E. Wilson, S.N. Suchard, and J.I.
   Steinfeld, Eds. (M.I.T. Press, Cambridge, MA, 1977), pp. 112-114.

3. A. Fontijn, "High Temperature Fast-Flow Reactor Studies of Elementary
   Reactions," High Temperature Metal Halide Chemistry, D.L. Hildenbrand and
   D.D. Cubicciotti, Eds. (The Electrochemical Society, Princeton, NJ, 1978),
   pp. 484-493.

A unique experimental method is described for providing information
on the kinetics of individual elementary reactions of neutral metallic species
as a function of temperature. This high-temperature fast-flow reactor (HTFFR)
technique has allowed the study of oxidation reactions of refractory metal
atom and metal oxide species from about 300 to 1900 K by a single experimental
method, thereby overlapping the temperature domains of traditional near room
temperature techniques and flames and shock tubes. The technique, some sig-
nificant results, and its extension to measurements on chemiluminescent and
electronic excitation quenching reactions are briefly reviewed. The signif-
icance of the results for practical systems is pointed out.

4. W. Felder and A. Fontijn, "HTFFR Kinetics Studies of Sn/N_2O, A Highly
   Efficient Chemiluminescent Reaction," The Journal of Chemical Physics
   69, 1112-1120 (1978).

High temperature fast-flow reactors (HTFFR) were used to study the
Sn/N_2O reaction from 300-950 K at pressures from 4 to 110 Torr. The observed
emissions are $SnO[a^3\Sigma^+(1)-X^1\Sigma^+]$ and $(b^3\Pi-X^1\Sigma^+)$. The photon yield of the form-
er system is 0.53 ± 0.26 independent of T, that of the latter $(5.9 \pm 2.9) \times$
$10^{-1}exp[-(1200 \pm 200)/T]$. Comparison of the photon yields of N_2O- in-excess
experiments, where [Sn] is measured in absorption, to experiments where Sn is
in excess allows determination of oscillator strengths for the ground electronic
states of Sn: $f[Sn(^3P_0)\ (286.4\ nm)] = 0.20 \pm 0.10$ and $f[Sn(^3P_1)\ (300.9\ nm)] =$
0.052 ± 0.026, in good agreement with literature values. At $T > 950$ K,
emission from $SnO(c-X^1\Sigma^+)$ and $(A^1\Pi-X^1\Sigma^+)$ is observed, apparently due to N_2O
decomposition followed by Sn/O_2 reaction. Quenching rate coefficients at $\approx$
900 K for SnO(a) are determined to be $k_Q^{N_2}(a) \leq 2.3 \times 10^{-16}$; $k_Q^{Ar}(a) \leq 4.0 \times$
10^{-16}; $k_Q^{N_2O}(a) \leq 4.0 \times 10^{-14}$; $k_Q^{Sn}(a) \leq 4.0 \times 10^{-12}$ ml molecule^{-1} s^{-1} based

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* Article contains no separate abstract. It is itself essentially a long
  abstract superseded by the later publications resulting from this work
  (especially publications 4, 7, and 8).

on $\tau_{rad}(a) \gtrsim 2.5 \times 10^{-4}$ s. For SnO(b) the data yield $\tau_b k_Q^{N_2}(b) = 4.8 \times 10^{-20}$; $\tau_b k_Q^{Ar}(b) \leq 2.0 \times 10^{-20}$; $\tau_b k_Q^{N_2O}(b) \leq 1.0 \times 10^{-17}$; $\tau_b k_Q^{Sn}(b) \leq 1.0 \times 10^{-15}$ ml molecule^{-1}. The overall $Sn(^3P_0)/N_2O$ reaction (production of all states) proceeds with a rate coefficient $(8.9 \pm 4.0) \times 10^{-13} exp[-(2260 \pm 180)/T]$ ml molecule^{-1}s^{-1}. Approximate overall rate coefficients are reported for $Sn(^3P_1)/N_2O$, $Sn(^3P_0)/NO_2$, and $Sn(^3P_{0,1})/O_2$.

5. A. Fontijn, "Studies of Elementary Reaction Kinetics of High-Temperature Species Using Optical Measurement Techniques," AeroChem TP-375, July 1978, Tenth Materials Research Symposium -- Characterization of High Temperature Vapors and Gases, J.W. Hastie, Ed. (The National Bureau of Standards, in press).

A unique experimental method is described for providing information on the kinetics of individual elementary reactions of neutral metallic species (free atoms and diatomic radicals) as a function of temperature. This high-temperature fast-flow reactor (HTFFR) technique has allowed the study of oxidation reactions of refractory metal atom and metal oxide species from about 300-1900 K by a single experimental method, thereby overlapping the temperature domains of traditional near room temperature techniques and flames and shock tubes. The technique, which uses absorption and fluorescence measurements of the consumption of the metallic species, allows for independent variation of temperature, pressure, reactant concentrations, and reaction time. Some significant results, and an extension to measurements on chemiluminescent and electronic excitation quenching reactions are discussed. A brief comparison is made to other techniques for obtaining information on homogeneous gas-phase reactions of such metallic species. Adaptation of the heated reactor technique to determine the temperature dependence of rate coefficients of elementary reactions of hydrocarbons using high-temperature photolysis (HTP) in a static mode is discussed.

6.* A. Fontijn and W. Felder, "High Temperature Flow Tubes - Generation and Measurement of Refractory Species," AeroChem TP-373, August 1978, Reactive Intermediates in the Gas Phase: Generation and Monitoring, D.W. Setser, Ed. (Academic Press, New York, in press).

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* This article does not contain an abstract; instead its Table of Contents, as it appeared in AeroChem TP-373 and given here, fulfills this function.

7. A. Fontijn and W. Felder, "HTFFR Kinetics Studies of the Ge/N_2O Chemi-luminescent Reaction," AeroChem TP-386, July 1979, The Journal of Chemical Physics, submitted.

    The reaction

$$Ge(4^3P_{0,1,2}) + N_2O \rightarrow GeO(X^1\Sigma^+, a^3\Sigma^+, b^3\Pi_1, A^1\Pi) + N_2 \qquad (1)$$
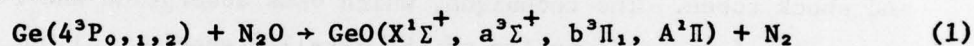
has been studied in a high-temperature fast-flow reactor (HTFFR) at temperatures from 475 to 920 K and pressures from 3 to 55 Torr. The following Ge removal rate coefficients were obtained (in units of ml molecule^{-1}s^{-1}):

$$k_1 Ge(^3P_0) = (1.7 \pm 0.3) \times 10^{-11} exp[-(470 \pm 60)/T]$$

$$k_1 Ge(^3P_1) = (8.1 \pm 1.3) \times 10^{-12} exp[(120 \pm 40)/T]$$

$$k_1 Ge(^3P_2) = (1.2 \pm 0.4) \times 10^{-11} exp[-(200 \pm 100)/T]$$

While these k are considerably higher than those observed in the Sn/N_2O reaction, the photon yields, Φ, are two to three orders of magnitude lower and, because of the resulting low chemiluminescence intensity, a complete kinetic expression could be obtained only for $\Phi(a)$:

$$\Phi(a) = (8.2 \pm 6.2) \times 10^2 \{1.3 \times 10^{-4} + 0.4 \times 10^{-21}[Ar]\}\{1 + 3.3 \times 10^{-15}[N_2O]\}^{-1} exp[-(2800 \pm 400)/T]$$

At $[Ar] = (3 \text{ to } 4) \times 10^{17}$ ml^{-1}, we obtain

$$\Phi(b) = (0.23 \pm 0.13)(1 + 2.6 \times 10^{-15}[N_2O])^{-1}\exp[-(4900 \pm 200)/T]$$

$$\Phi(A) = (0.033 \pm 0.025)(1 + 2.8 \times 10^{-16}[N_2O])^{-1}\exp[-(3800 \pm 380)/T]$$

At 545 K the following Stern-Volmer coefficients, $\tau k_Q^{N_2O}$, for quenching by N_2O were obtained (in ml molecule^{-1}), GeO(a):$(3.3 \pm 0.9) \times 10^{-15}$; GeO(b):$(2.6 \pm 1.4) \times 10^{-15}$; GeO(A):$(2.8 \pm 1.4) \times 10^{-16}$. It is shown that Reaction (1) is not an elementary reaction and a more detailed mechanism is proposed which, similar to that of Sn/N_2O, involves preferential reaction through the $^3P_1$ state and intermediate formation of a GeO* reservoir state from which the emitting GeO states are formed collisionally. The trends in the Group IVA element/N_2O reaction kinetics are discussed.

8. D.M. Manos and A. Fontijn, "Additional HTFFR Observations on Chemi-luminescent Sn-Oxidizer Reactions," AeroChem TP-387, July 1979, The Journal of Chemical Physics, submitted.

Product quenching of $SnO(a^3\Sigma)$ from the Sn/N_2O reaction was studied in a high-temperature fast-flow reactor (HTFFR) at 850 K. For Sn as the limiting reagent these studies yield the Stern-Volmer expression $\Phi_0(a-X)/\Phi(a-X) = 1.0 + 3.9(\pm \sigma = 0.2) \times 10^5 [Sn]_{initial}/[Ar]$. A mechanism is advanced by which the precursor state of $SnO(a^3\Sigma)$ can either transfer to this emitting state by collisions with the bath gas (Ar) or be quenched by other SnO molecules in unspecified states.

At 360 K qualitative observations were made of the Sn/O, $Sn/O/O_2$, and Sn/O_2 reactions, which show that these reactions populate $SnO(a^3\Sigma, b^3\Pi, c,$ and $A^1\Pi)$ and that O_2 is an efficient quencher of $SnO(a^3\Sigma)$. It is shown that the c-X and A-X emissions from Sn/N_2O at elevated temperatures may be attributed to reaction of Sn with O and/or O_2 from N_2O decomposition.

III. SOME CHEMICAL ELECTRONIC TRANSITION LASER IMPLICATIONS

Articles 7 and 8 of Section II contain the cumulative conclusions of the present three year study and from them the most significant CETL implications can be drawn.

A. THE PROMISE AND LIMITATIONS OF THE Sn/N₂O REACTION

The final Section (IV.B) of Article 7 compares all available knowledge of the Group IVA element/N_2O reactions. Information on C, Si, Ge, Sn, and Pb is considered. Sn appears unique in that its N_2O reaction has a photon

yield ϕ (which equals the branching ratio in the absence of quenching) several orders of magnitude higher than the other members of the series ($\phi(a)$ = 0.5 ± 0.26 for $SnO(a^3\Sigma)$). Moreover, there is no measurable quenching of this state by either reactants or bath gases, cf., the abstract of Article 4, while the emitting GeO states all are quenched efficiently by N_2O.

In Section III of Article 8 the effect of product quenching on the $SnO(a^3\Sigma)$ photon yield from the Sn/N_2O reaction in Ar bath gas is investigated. Such quenching is observed. It is concluded that this quenching actually reflects quenching by other SnO molecules of SnO in a precursor state to the $a^3\Sigma$ state. The degree of quenching depends on the initial [Sn] (for Sn as the limiting reagent) and on the bath gas concentration, since collisions with the bath gas are needed to transfer SnO from the reservoir state to the $a^3\Sigma$ state.

The steady-state kinetic equation for this mechanism shows that $\phi(a)$ can be described as a function of the kinetic parameters f_a, z, and u, which are defined as: f_a is the fraction of collisions between the precursor state and Ar that lead to formation of $SnO(a^3\Sigma)$, z is the product of the total Sn/N_2O rate coefficient, the initial [N_2O], and the radiative lifetime for spontaneous emission of the $a^3\Sigma$ state, and u is proportional to $[Sn]_{i(nitial)}/[Ar]$. As derived in the article:

$$\phi(a) = \frac{f_a}{(1 - z)u} \ln\left(\frac{1 + u}{1 + zu}\right) \tag{A}$$

In a laser cavity the effective radiative lifetime would be

$$\tau_{rad} = 1/(A_\nu + I_\nu B_\nu)$$

where A_ν, B_ν are the Einstein transition probabilities and I_ν is the intra-cavity intensity. For power densities beyond threshold the second term of the denominator will dominate and $\tau_{rad} = \tau_{stimulated} \ll \tau_{spontaneous}$. Thus the parameter z in Eq. (A) can be neglected and

$$\phi(a) = f_a \frac{1}{u} \ln(1 + u) \tag{B}$$

Equation (B) has its maximum values (= f_a) at u = 0; hence in order to maximize [$SnO(a^3\Sigma)$] in a practical device, the ratio $[Sn]_i/[Ar]$ must be maintained as small as possible. This leads to some difficult practical requirements since we measured u to be large: $\approx 6.5 \times 10^5 [Sn]_i/[Ar]$. Calculations

were performed several years ago at AeroChem* to investigate the use of the Sn/N_2O reaction in a free jet laser. It was found that in order to provide a gain of $\approx 0.1\% \ cm^{-1}$, $[Sn] \approx 1 \times 10^{16} \ ml^{-1}$ would be required. This would require large Ar densities ($[Ar] \approx 6.5 \times 10^{21} \ ml^{-1}$) in order to reduce u to 1 and hence product quenching to an essentially negligible level: $\Phi/\Phi_0 = 0.69$. Such Ar densities appear rather high for a practical situation. Of course, other bath gases may require different concentrations.

A proviso to be made is that these product quenching studies were done at [Ar] from 1.7×10^{17} to $4.6 \times 10^{17} \ ml^{-1}$. Extrapolation to $[Ar] = 6.5 \times 10^{21}$ is rather a long way and studies at intermediate pressures are in order. We understand that gain experiments at higher pressures are in progress at Bell Aerospace; these may indeed offer hope for a practical Sn/N_2O based laser. However, we have been unable to obtain any details. If further scrutiny of their results confirms such promise, details on the product quenching mechanism would appear to be needed; for example, experiments to establish the state identity of the quenchant as well as the precursor state should then be made.

B. REACTIONS OF Sn WITH OTHER OXIDIZERS

In Section IV of Article 8 some studies of a more qualitative nature, at 360 K, of Sn with O-atoms, O_2, and combinations thereof are discussed. The O-atom reaction does indeed produce maximum SnO (a-X and b-X) intensities comparable to those obtained at 850 K from Sn/N_2O at similar [Sn]. However, these studies also showed that O_2 is an efficient quencher of the SnO(a) emissions. These O and O_2 reactions do, contrary to the Sn/N_2O reaction, also populate the higher-lying SnO c and A states; however, the intensities of the resulting emissions are comparable to those of b-X, an order of magnitude lower than achievable for a-X emission. Since O free of O_2 does not appear to be a reagent practical for an operational laser, these reagents do not seem attractive for further investigations in the CETL context.

This work does demonstrate the necessity of keeping O_2 out of the cavity of an Sn/N_2O based laser. Other oxygen oxidizers could, of course, be more useful than the O, O_2 combinations.

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*A Fontijn, W. Felder, and R.K. Gould, "Experiments for the Development of an Sn/N_2O Electronic Transition Chemical Laser," AeroChem Proposal P-340 to DARPA/AFWL, February 1976, Section IV. Copies of this proposal, or this section, can be reproduced upon request of cognizant government agencies.

IV. CUMULATIVE CHRONOLOGICAL LIST OF PRESENTATIONS AND CONTACTS

Presentations on our work were given at:*

1. The 11th Informal Conference on Photochemistry, National Bureau of Standards, Gaithersburg, MD, June 1976.

2. Third Summer Colloquium on Electronic Transition Lasers, Snowmass, CO, September 1976.

*3. School of Chemical Engineering, Cornell University, Ithaca, NY, October 1976.

4. Fall Meeting, Eastern Section of the Combustion Institute, Drexel University, Philadelphia, PA, November 1976.

*5. Brookhaven National Laboratory, Upton, L.I., NY, January 1977.

*6. Laser and Applied Physics Seminar, Princeton University, Princeton, NJ, May 1977.

7. AFOSR Contractors Meeting on Laser-Related Research, Kirtland AFB, Albuquerque, NM, May 1977.

8. Third IUPAC Plasma Chemistry Meeting, Limoges, France, July 1977.

*9. 174th American Chemical Society National Meeting, Chicago, IL, August 1977.

10. Electrochemical Society Symposium on High Temperature Metal Halide Chemistry, Atlanta, GA, October 1977.

*11. Physics Department, Georgia Institute of Technology, Atlanta, GA, October 1977.

*12. Quantum Institute, University of California, Santa Barbara, CA, October 1977.

*13. North Jersey Section, American Chemical Society, Newark, NJ, November 1977.

*14. Chemistry Department, Princeton University, Princeton, NJ, December 1977 (as part of a kinetics course).

*15. Chemical Engineering Department, Princeton University, Princeton, NJ, April 1978.

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* Invited presentations are marked with an asterisk.

*16.   Gordon Research Conference on High Temperature Chemistry.
Brewster Academy, Wolfeboro, NH, August 1978.

17.   Tenth Materials Research Symposium: Characterization of High
Temperature Vapors and Gases, National Bureau of Standards, Gaithersburg,
MD, September 1978.

With the exception of presentations 1 and 4, given by Dr. W. Felder,
the presentations were made by Dr. A. Fontijn.

Frequent information contacts have been maintained with Air Force
Weapons Laboratory personnel. The principal contacts there were: Lt. Col.
D.S. Olson, Maj. R.R. Bousek, Maj. C. Dymek, Dr. D.J. Benard, and Dr. S.J.
Davis.

V.   RESEARCH PARTICIPANTS

In addition to the principal investigator, Dr. A. Fontijn, the following
AeroChem personnel contributed significantly to this work: Dr. W. Felder,
Dr. D.M. Manos, J.J. Houghton, and W.R. Frenchu. The former two are members
of the AeroChem research staff, and latter two of technical support staff.
Mr. Frenchu is now at RCA David Sarnoff Laboratories.